Mixed-ligand complexes of copper VII. Polarographic studies on copper–carboxylate–aminocarboxylate complexes

V V RAMANUJAM* and U KRISHNAN

Department of Inorganic Chemistry, A.C. College Buildings, Madras 600 025, India

Abstract. The formation constants of mixed-ligand complexes with hetero donors of the type CuAB where A is a carboxylic acid such as lactic acid or oxalic acid and B is an α- or β-amino acid are studied by polarography. The mixed-ligand stabilisation constant clearly indicates the preferred formation of copper(II) mixed-ligand complexes with hetero donors over homo donors. The other driving forces leading to the favoured formation of mixed-ligand complexes are also discussed.

Keywords. Mixed-ligand complexes; copper(II); lactic acid; oxalic acid; amino acid.

1. Introduction

The polarographic method widely used to study single-ligand systems, has however been rarely applied to mixed-ligand complexes. It was first used for the study of mixed-ligand complexes by Schaap and McMasters (1961) by extending the method of DeFord and Hume (1951) to determine the consecutive overall formation constants of single-ligand complexes. Recently Sigel (1975) and Krishnan (1980) have reiterated that copper(II) prefers hetero donors over homo-donors in mixed-ligand complexes. The results obtained from the polarographic technique for some of the mixed-ligand complexes of copper(II) with biologically important bidentate ligands with hetero donor atoms are presented in this paper.
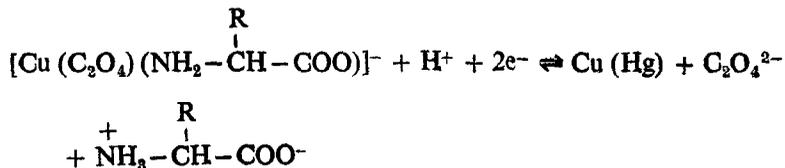
2. Experimental

2.1. *Copper-oxalate-aminocarboxylate complexes*

2.1a. *Effect of pH.* Polarograms were recorded for solutions containing a constant concentration of copper(II) (3.98×10^{-4} M) and a varying large excess of oxalate and/or aminocarboxylate. At pH values near 5 the dioxalatocuprate (II) is the predominant species present and at pH above 8 only diglycinatocopper (II) is present. In the intermediate pH range of $5.4–6.8$, both mixed-ligand complexes and binary complexes are present as inferred from the magnitude of

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* To whom all correspondence should be made.

the $\triangle E_{1/2}$. This is in accordance with the findings from our spectrophotometric studies Ramanujam and Krishnan (1980) where λ_{max} is the deciding factor. The plot of $E_{1/2}$ *vs* pH in the pH range of 5·4–6·8 is linear as seen from figure 1 and the slope of these are about 0·03 V, showing the involvement of one proton in the electrode process. This would protonate the $-NH_2$ group of the amino-carboxylate ion. The electrode process may be represented as follows :

$$[Cu\,(C_2O_4)\,(NH_2\overset{\underset{\displaystyle R}{|}}{-CH}-COO)]^- + H^+ + 2e^- \rightleftharpoons Cu\,(Hg) + C_2O_4{}^{2-}$$

$$+ \overset{+}{NH_3}\overset{\underset{\displaystyle R}{|}}{-CH}-COO^-$$

2.1b. *Effect of ligand concentration on $E_{1/2}$.* To determine the formula of the mixed-ligand complex the method of Lingane (1941) used for the binary complexes was modified. Keeping the pH constant (at the preselected value) and the concentration of one of the ligands (say, secondary ligand) was varied. From the plot of $E_{1/2}$ *vs* $-$log [secondary ligand], the value of the slope P, gives the number of secondary ligands coordinated to 1 : 1 copper(II)-primary ligand complex.

As it is experimentally much easier to hold the oxalate concentration constant and vary the aminocarboxylate concentration, than *vice versa*, the $E_{1/2}$ *vs* $-$log [secondary ligand] plot is constructed with respect to the aminocarboxylate ion
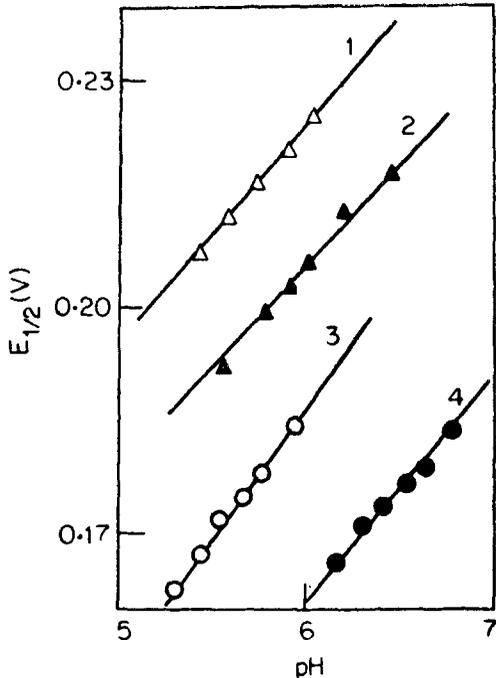

Figure 1. Copper-oxalate-aminocarboxylate complexes. Plot of $E_{\frac{1}{2}}$ vs pH
1. [Cu (ox) (gly)].   2. [Cu (ox) (ala)].   3. [Cu (ox) (ser)].   4. [Cu (ox) (bala)].

concentration. As a representative system such a curve for [Cu (ox) (gly)]*
at pH 5·85 and a constant oxalate concentration of 0·110 M is shown in figure 2.
The slope of this plot is 0·028 corresponding to $P = 1$, indicating clearly that
only one glycinate group is added to the 1 : 1 copper-oxalate complex. The
same formula was arrived at by Ramanujam and Krishnan (1980) from spectro-
photometric studies.

The formation constants obtained for all the mixed-ligand complexes by the
method of Schaap and McMasters (1961) are found to be fairly constant over the
pH range at which linear curves are obtained for the $E_{1/2}$ vs pH plot (figure 1).
The values obtained closely agree with those obtained from spectrophotometric
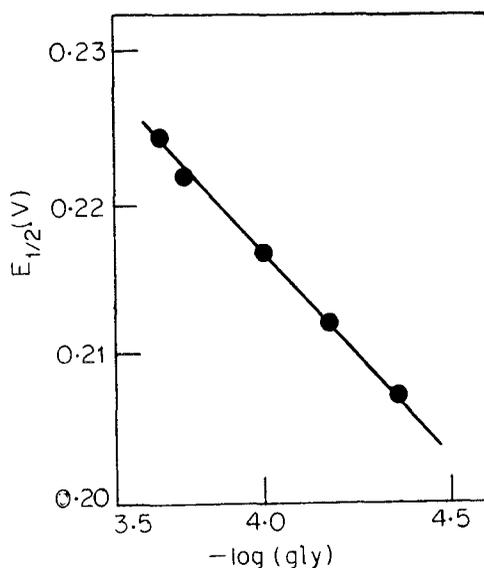studies as can be seen from table 1.

Figure 2. Copper-oxalate-glycinate complex. Effect of glycinate concentration on
E_i at pH = 5·85 and $ox = 0·110$ M.

Table 1. Copper-oxalate-aminocarboxylate complexes.

	Polarography		Spectrophotometry*
Complex	log β	log X	log β
[Cu (ox) (gly)]	12·93 ± 0·06	1·48	12·90 ± 0·05
[Cu (ox) (ala)]	12·79 ± 0·05	1·29	12·67 ± 0·18
[Cu (ox) (ser)]	12·06 ± 0·06	0·90	12·08 ± 0·03
[Cu (ox) (bala)]	11·87 ± 0·04	1·84	11·72 ± 0·16

* Values of log β from Ramanujam and Krishnan (1980).

* Abbreviations: ala = α-alaninate; am = aminocarboxylate; bala = β-alaninate; en = ethylene-
diamine; gly = glycinate; lact = lactate; ox = oxalate; pn = 1,3-propylenediamine and ser = serinate.

The mixed-ligand stabilization constant, log X is calculated from the disproportionation reaction such as shown below :
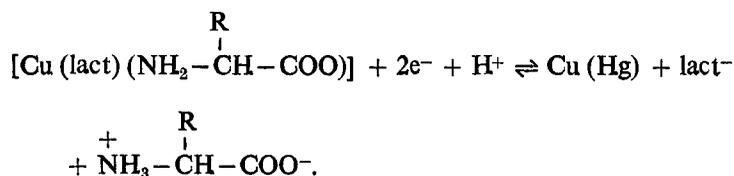
$$[Cu\,(ox)_2] + [Cu\,(am)_2] \rightleftharpoons [2\,Cu\,(ox)\,(am)]$$
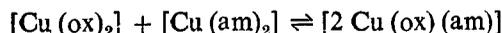
$$X = \frac{[Cu\,(ox)\,(am)]^2}{[Cu\,(ox)_2]\,[Cu\,(am)_2]}$$

$$\log X = 2\log \beta_{Cu\,(ox)\,(am)} - \{\log \beta_{Cu\,(ox)_2} + \log \beta_{Cu\,(am)_2}\}.$$

The log X value proposed by Sharma and Schubert (1969) on statistical grounds is 0·6 and an observed value of log X greater than 0·6 indicates favoured formation of the mixed-ligand complexes over binary complexes. The high log X values listed in table 1 show that the mixed-ligand complexes are highly favoured.

The variation of $E_{1/2}$ with pH was studied for the mixed-ligand complexes of copper(II) with lactate and aminocarboxylate in the pH range 5·2–6·4 as described earlier for the [Cu (ox) (am)] systems. Linear plots are obtained with a slope of about 0·03 V. This value corresponds to one proton which is inferred to protonate the $-NH_2$ group of the aminocarboxylate ion as shown below :

$$[Cu\,(lact)\,(NH_2 - \overset{\overset{\displaystyle R}{|}}{CH} - COO)] + 2e^- + H^+ \rightleftharpoons Cu\,(Hg) + lact^-$$

$$+ \overset{+}{N}H_3 - \overset{\overset{\displaystyle R}{|}}{CH} - COO^-.$$

Studies on the effect of varying the aminocarboxylate ion concentration on $E_{1/2}$ at pH 5·60 and at a lactate ion concentration of 0·25 M showed the composition of the mixed-ligand complex to be [Cu (lact) (am)].

The overall formation constant of these mixed-ligand complexes calculated over the pH range of 5·2–6·4 is fairly constant. The values obtained here are in good agreement with those of pH-metric and spectrophotometric studies as can be seen from table 2. The log X values for all these complexes are seen to be high. The preference for mixed-ligand complexes with one five- and one six-membered ring over two five-membered rings is clearly brought out in all cases where β-alanine is one of the ligands and forms a six-membered ring.

The log X value among the α-amino acids varies in the order glycinate > α-alaninate > serinate. This trend may be due to steric factors, namely, the presence of more substituent groups in the chelating ligands.

The log X values of these mixed-ligand complexes where three donor sites are oxygen atoms and one is a nitrogen atom are higher than those having only oxygen or nitrogen as donors. The log X values of some mixed-ligand complexes of copper(II) with homo and hetero donor atoms calculated from polarographic data are listed in table 3.

In the case of [Cu (lact) (am)] the complex is neutral. The formation of a neutral complex appears to be a strong driving force for the favoured formation of the mixed-ligand complexes. This is one of the reasons for the enhanced value of log X for [Cu (lact)(am)] compared to [Cu(ox)(am)] with a uninegative charge.

Table 2. Copper-lactate-aminocarboxylate complexes.

Complex	Polarography log β	log X	pH-metry @ log β	Spectrophotometry @ log β
[Cu (lact) (gly)]	$10 \cdot 83 \pm 0 \cdot 04$	$2 \cdot 51$	$10 \cdot 91 \pm 0 \cdot 02$	$10 \cdot 74 \pm 0 \cdot 06$
[Cu (lact) (ala)]	$10 \cdot 70 \pm 0 \cdot 05$	$1 \cdot 66$	$10 \cdot 65 \pm 0 \cdot 14$	$10 \cdot 22 \pm 0 \cdot 07$
[Cu (lact) (ser)]	$10 \cdot 09 \pm 0 \cdot 03$	$1 \cdot 67$	$10 \cdot 02 \pm 0 \cdot 07$	$9 \cdot 76 \pm 0 \cdot 07$
[Cu (lact) (bala)]	$9 \cdot 74 \pm 0 \cdot 06$	$2 \cdot 81$	$9 \cdot 97 \pm 0 \cdot 11$	$9 \cdot 68 \pm 0 \cdot 08$

@ Values of log β from Krishnan (1980).

Table 3. Log X values of some of the mixed-ligand complexes of copper(II) with homo and hetero donors from Krishnan (1980).

Complex	Donors Oxygen	Nitrogen	log X
[Cu (lact) (ox)]	4	0	$0 \cdot 43$
[Cu (ox) (gly)]	3	1	$1 \cdot 48$
[Cu (lact) (en)]	2	2	$2 \cdot 62$
[Cu (en) (gly)]	1	3	$1 \cdot 71$
[Cu (en) (pn)]	0	4	$1 \cdot 17$

In the case of lactate complexes, the studies indicate coordination of the hydroxyl group in its unionised form. Martin and Paris (1963) and Griesser *et al* (1968) have also indicated the participation of the hydroxyl group in coordination in mixed-ligand complexes. Such a coordination is weaker than in its deprotonated form. It is of great importance in biological processes such as metal-enzyme action, as it allows a rapid rearrangement of the complexes necessary for the enzyme to act as a catalyst.

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